

**PATENT ABSTRACTS OF JAPAN**

(11)Publication number : 2000-191874

(43)Date of publication of application : 11.07.2000

(51)Int.Cl.

C08L 29/04  
C08K 3/00

(21)Application number : 10-368756

(71)Applicant : NIPPON SYNTHETIC CHEM IND CO  
LTD:THE

(22)Date of filing : 25.12.1998

(72)Inventor : INOUE KAORU  
NAITO TAMAHIDE**(54) PREPARATION OF RESIN COMPOSITION****(57)Abstract:**

**PROBLEM TO BE SOLVED:** To obtain a composition which is excellent in productivity, gas barrier properties and appearance properties by melting and mixing a saponified ethylene-vinyl acetate copolymer having a specific water content and a water-swelling layered inorganic compound.

**SOLUTION:** A saponified ethylene-vinyl acetate copolymer(EVOH) having a water content of 25-50 wt.% is used. An EVOH having an ethylene content of 5-60 mol% and a degree of saponification of 90 mol% is preferable. A smectite, especially a montmorillonite, is preferable as a water-swelling layered inorganic compound. A water-swelling fluorine mica mineral is also preferable. The swelling force of the water-swelling layered inorganic compound is preferably at least 30 ml/2 g at 20°C against the mixed solvent of water/alcohol: 70/30 (in weight). Melting and mixing temperature is preferably not more than 100°C. The amount of the water-swelling layered inorganic compound is preferably 2-20 pts.wt. against 100 pts.wt. of EVOH (solid content).

## \* NOTICES \*

JP0 and INPIT are not responsible for any damages caused by the use of this translation.

- 1.This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.\*\*\*\* shows the word which can not be translated.
- 3.In the drawings, any words are not translated.

---

## DETAILED DESCRIPTION

---

[Detailed Description of the Invention]

[0001]

[Field of the Invention]This invention relates to the manufacturing method of the resin composition excellent in productivity, or gas barrier property and appearance properties in more detail about the resin composition of an ethylene-vinylacetate copolymer saponification thing (it is hereafter written as EVOH).

[0002]

[Description of the Prior Art]Generally, EVOH is excellent in transparency, antistatic property, oil resistance, solvent resistance, gas barrier property, a smell retaining property, etc., and is thermoplastics in which melt molding is possible.

It is used for various wrapping uses, such as food packing.

However, gas barrier property and a mechanical physical property change with change of the environment of external humidity and temperature a lot, and EVOH has the fault that gas barrier property falls, under the environment of high humidity.

[0003]On the other hand, it is indicated by recent years that the mixed material of EVOH and a water swelling inorganic compound is capturing the spotlight for the purpose of the improvement of gas barrier property, for example, mixes EVOH and water swelling phyllosilicate under existence of water at JP,5-39392,A. To JP,10-158412,A, the manufacturing method of the heating process which heats the vinyl alcohol copolymer which added argillite and obtains melt, the mixing step which kneads this melt, and the clay composite material which becomes this melt from the hydrogenation process of adding water is indicated.

[0004]

[Problem(s) to be Solved by the Invention]However, as a result of this invention person's etc. inquiring in detail, in the above-mentioned JP,5-39392,A indication art. In order to mix EVOH with water swelling phyllosilicate in the state of a solution, the process dissolved in a solvent is required, or EVOH. In order to supply water swelling phyllosilicate under existence of water and also to add the water/alcohol solution of EVOH, It became clear that will be easy to generate what is called insoluble, it could not distribute to homogeneity, and time most for carrying out uniform dispersion would be needed, and productivity worsened.

[0005]In order to be stabilized and to acquire good gas barrier property, In spite of swelling argillite enough in water, in JP,10-158412,A indication art.Since the quantity of the water to add was ten or less weight

sections to EVOH100 weight section, showy \*\* which argillite cannot fully swell, but is stabilized and is mixed uniformly becomes there is not less, and it became clear that good gas barrier property or appearance properties could not be acquired. Then, under such a background, it aims at providing the manufacturing method of the resin composition which was excellent in productivity and also was excellent in gas barrier property or appearance properties by this invention.

[0006]

[Means for Solving the Problem]As a result of repeating research wholeheartedly in light of the above-mentioned circumstances, this invention persons found out that a manufacturing method of a resin composition which carries out melting mixing of EVOH of 25 to 50 % of the weight of water content and the water swelling laminar inorganic compound agreed for the above-mentioned purpose, and completed this invention.

[0007]

[Embodiment of the Invention]Below, this invention is explained in detail. as EVOH used for this invention -- 5-60 mol of ethylene content % -- desirable -- 10-60-mol %. furthermore -- desirable -- the degree of saponification of 20-55-mol % and a vinyl acetate component -- more than 90 mol % -- if the thing beyond 95 mol % is used suitably preferably, an ethylene content becomes insufficient [ less than / 5 mol % / a water resisting property ] and 60-mol % is exceeded on the other hand, gas barrier property falls and it is not desirable. The degree of saponification becomes insufficient [ less than / 90 mol % / a water resisting property ], and is not preferred.

[0008]As a melt index (MI) of this EVOH, 1-100g/10 minutes (210 \*\*, 2160g of load) are preferred, and is 2-50g/10 minutes (210 \*\*, 2160g of load) more preferably. If load becomes large too much, and this melt index (MI) will interfere with processing and exceeds 100g/10 minutes in 1g/less than 10 minutes at the time of melting processing, viscosity becomes low too much at the time of melting, a lappet happens, shaping of a film etc. becomes impossible, and it is not desirable.

[0009]Propylene of further a small quantity [ EVOH / this ], isobutene, alpha-octene, Alpha olefins, such as alpha-dodecen and alpha-octadecene, unsaturated carboxylic acid, or its salt, partial alkyl ester, perfect alkyl ester nitril amide and anhydride, It does not interfere, even if comonomers, such as unsaturation sulfonic acid or its salt, a vinyl silane compound, VCM/PVC, and styrene, are included. In the range of this invention, even if urethane-izing, acetalization, cyanoethylation, acetalization, cyanoethylation "post-denaturation", etc. are used, it does not interfere.

[0010]In this invention, the above-mentioned EVOH is made to contain water and 25 to 50 % of the weight of water content needs to be more preferably referred to as 25 to 40% of the weight of EVOH. If this water content does not carry out micro-disperse in EVOH in order that a water swelling laminar inorganic compound may not fully swell at less than 25 % of the weight, a gas-barrier-property improvement effect is not acquired but 50 % of the weight is exceeded, a lot of water will blow off, it will become impossible to process it from EVOH at the time of processing, and the effect of this invention will not be demonstrated.

[0011]Especially as a method of making EVOH containing water, although not restricted, as a method which it is preferred to make water contain uniformly and requires it into EVOH, The method of depositing the solution of EVOH underwater, fully rinsing, removing a solvent, and making water containing, the method of processing EVOH in pressurized hot water for about 1 to 3 hours, the method of depositing the paste after saponification of an ethylene-vinylacetate copolymer underwater at the time of manufacture of

EVOH, and making water contain, etc. are mentioned. The method of depositing the paste after saponification of an ethylene-vinylacetate copolymer underwater even especially in inside at the time of EVOH manufacture is used preferably. Only by mixing EVOH and water, since water is not uniformly contained in EVOH, the effect of this invention cannot be demonstrated.

[0012]As a water swelling laminar inorganic compound used for this invention, Without being restricted especially Argillite, such as a smectite and a vermiculite, Synthetic mica etc. are mentioned and montmorillonite, beidellite, nontronite, saponite, hectorite, a sauconite, a SUCHIBUN site, etc. are mentioned as an example of the former smectite. These may be natural things or could be compounded. Montmorillonite is preferred also the inside of these or a smectite, especially in it. Water swelling fluoride mica system minerals, such as Na-type fluoride 4 silicon mica, a Na-type TENIO light, Li type TENIO light, and Na-type hectorite, etc. are used preferably.

[0013]The swelling power of this water swelling laminar inorganic compound receives the partially aromatic solvent of water/alcohol =70 / 30 (weight ratio) in 20 \*\*, It is desirable, and it becomes insufficient [ 2 g / gas barrier property ] in less than 30ml /that not less than 40ml/2 g not less than 30ml/2 g is not less than 50ml/2 g still more preferably preferably, and it is not preferred. The swelling power of a water swelling laminar inorganic compound is a Japanese bentonite industrial meeting. It is measured by a standard-testing-method constant volume method.

[0014]It is the feature to carry out melting mixing of above-mentioned EVOH of 25 to 50 % of the weight of water content and water swelling laminar inorganic compound in this invention, and, as for the melting mixing temperature at this time, it is preferably preferred to choose out of the range of 70-90 \*\* 100 \*\* or less. If this temperature exceeds 100 \*\*, a lot of water will be emitted from resin, EVOH is no longer mixed with a water swelling laminar inorganic compound, and it is not desirable.

[0015]As for the quantity of the water swelling laminar inorganic compound by which melting mixing is carried out, it is preferred that it is two to 20 weight section to EVOH100 weight section (solid content), and it is three to 10 weight section more preferably. In less than the amount part of duplexes, there are few improvement effects of gas barrier property, if this quantity exceeds 20 weight sections, the appearance of molded products, such as a film, gets worse and it is not preferred.

[0016]Although not restricted in particular about melting mixing, EVOH (hydrous EVOH) of 25 to 50 % of the weight of the above-mentioned water content is supplied to a twin screw extruder, for example, Melting is carried out at the temperature of 100 \*\* or less, and the above-mentioned water swelling laminar inorganic compound is added there, and also it kneads, and the method of mixing hydrous EVOH and a water swelling laminar inorganic compound is mentioned. After carrying out melting mixing of the above-mentioned hydrous EVOH and the water swelling laminar inorganic compound in this way, it dries until water content will be 0.1 to 0.3% of the weight preferably 0.5 or less % of the weight if needed, and the target resin composition is obtained.

[0017]within the limits from which the purpose of this invention is not prevented in this invention -- other thermoplastics (polyolefine.) Ethylene glycol, such as polyamide, polyester, polystyrene, and EVOH, It is also possible to blend suitably plasticizers, such as propylene glycol and glycerin, a heat stabilizing agent, an ultraviolet ray absorbent, an antioxidant, colorant, inorganic matter and an organic bulking agent (except for a water swelling laminar inorganic compound), a drier, a spray for preventing static electricity, lubricant, an antimicrobial agent, etc. Metal salt of a hydrotalcite system compound, a hindered phenol system or a

hindered amine system thermostabilizer, and high-class aliphatic carboxylic acid can also be added as an antigelling agent.

[0018]The resin composition obtained with the manufacturing method of this invention in this way is used abundantly at the use of a molded product, and by melt molding etc. It is fabricated by a pellet, a film, a sheet, a container, textiles, a stick, a pipe, various mold goods, etc., and melt molding can also be again presented using these grinding articles (when carrying out the reuse of the recovery article etc.) and pellets. As melt molding, extrusion methods (T-die extrusion, inflation extrusion, blow molding, melt spinning, variant extrusion, etc.) and injection molding process are mainly adopted. Melt molding temperature is chosen from the range of 150-250 °C in many cases.

[0019]Although the resin composition obtained with the manufacturing method of this invention can be used for the molded product like \*\*\*\*, it is preferred to use at least for one side of the layer which especially consists of this resin composition as a layered product which laminates a thermoplastic resin layer, and a layered product suitable for practical use is obtained. In manufacturing this layered product, other substrates are laminated to one side or both sides of a layer of a resin composition which are acquired by the manufacturing method of this invention, but as a laminating method, the following methods are mentioned, for example. However, it is not limited to these.

[0020]The water-alcoholic (or solvent) content solution of a solution coating method this resin composition \*\* Mai Ya Bar, A thermoplastic resin film is coated by publicly known methods, such as the roller coating methods, such as photogravure and a reverse roll method, a spray coating method, and the dip-coating method, and a layered product is produced. Then, desiccation is performed by a publicly known method. If an example is given, drying temperature should just heat 40-180 °C 5 seconds - about 5 minutes at about 60-140 °C preferably. What is necessary is just to carry out until volatile matter content will usually be 2 or less % of the weight although the volatile matter content (water, alcohol, or solvent) in a coat is removed in this desiccation. In order to raise the adhesive strength of the resin composition layer obtained with the manufacturing method of this invention, and a thermoplastic resin film, the coat of the usual anchor coat agents (a polyurethane system, a polyester system, etc.) may be beforehand carried out on a film.

[0021]\*\* Carry out melting extrusion of the thermoplastics to the film of the resin composition obtained with the manufacturing method of the extrusion coating Homoto invention, and a sheet, and produce a layered product. Melting extrusion of the resin composition of this invention is conversely carried out to substrates, such as thermoplastics, and a layered product is produced.

[0022]\*\* Co-extrude the resin composition obtained with the manufacturing method of the co-extrusion Homoto invention, and other thermoplastic thing resin, and produce a layered product. As other party resin in co-extrusion, straight-chain-shape low density polyethylene, low density polyethylene, Medium density polyethylene, high density polyethylene, an ethylene-vinylacetate copolymer, An ionomer, ethylene propylene rubber, an ethylene-acrylic ester copolymer, Polypropylene, a propylene-alpha olefin (alpha olefin of carbon numbers 4-20) copolymer, Polyolefin system resin of broad sense, such as independent or an independent or thing of copolymers or these olefins of olefins, such as polybutene and a polypentene, which carried out graft denaturation of the copolymer with unsaturated carboxylic acid or its ester, Polyester, polyamide, copolymerization polyamide, polyvinyl chloride, a polyvinylidene chloride, Acrylic resin, polystyrene system resin, vinyl ester resin, a polyester elastomer, a polyurethane elastomer, chlorinated polyethylene, chlorinated polypropylene, EVOH, etc. are mentioned. Also in the above,

polypropylene, polyamide, polyethylene, an ethylene-vinyl acetate system copolymer, polystyrene, polyethylene terephthalate, etc. are preferably used from a point of the ease of co-extrusion film production, and the practicality of film properties (especially intensity).

[0023]In co-extrusion, to the resin composition obtained with the manufacturing method of this invention Thermoplastics, The resin composition obtained by thermoplastics with the manufacturing method of this invention may be blended, or the resin which raises the adhesion of both stratification planes may be blended at least with one side of the resin composition and thermoplastics which were obtained with the manufacturing method of this invention.

[0024]\*\* Laminate the film of the resin composition obtained with the manufacturing method of the dry laminate Homoto invention, a sheet, and the film of other substrates and a sheet using publicly known adhesives, such as an organic titanium compound, an isocyanate compound, a polyester system compound, and a polyurethane compound, and produce a layered product. The \*\* co-extruding method is advantageous in respect of processability also in the above.

[0025]Molded products, such as a film and a sheet, are once obtained from the resin composition obtained with the manufacturing method of this invention, When the extrusion coat of other substrates is carried out to this or the film of other substrates, a sheet, etc. are laminated using adhesives, It is usable in substrates (paper, a metallic foil, uniaxial stretching, a biaxially oriented plastic film or a sheet, textile fabrics, a nonwoven fabric, \*\*\*\*\*, a woody side, etc.) arbitrary in addition to the aforementioned thermoplastics.

[0026]When setting a (a1, a2, ...) and other substrates, for example, a thermoplastic resin layer, to b (b1, b2, ...) for the layer of the resin composition obtained with the manufacturing method of this invention as lamination of a layered product, If it has a film, a sheet, and the shape of a bottle, only not only in the two-layer structure of a/b, b/a/b, a/b/a, a1/a2/b, a/b1/b2, b2/b1-/a/b1 / b2 grade, and arbitrary combination are possible, and arbitrary combination, such as a bimetal type, a core (a)-sheath (b) type, a core (b)-sheath (a) type, or an eccentric sheath-core type, is possible for a and b in filament shape.

[0027]Although the above-mentioned resin composition or a layered product is used for the thing of various shape as it is, it is preferred to perform stretching treatment for a physical-properties improvement, and about this extension, it may be any of uniaxial stretching and biaxial stretching and is [ having extended high magnification way-wise / physical properties / as much as possible ] good.

[0028]What has draw magnification high as an extension method, such as deep drawing shaping and vacuum forming besides being the roll extending method, the tenter extending method, the tubular extending method, the extension blowing method, etc., is employable. In the case of biaxial stretching, any method of a simultaneous biaxial-stretching method and a serial biaxial-stretching method is employable.

80-170 \*\* of extension temperature is preferably chosen from the range of about 100-160 \*\*.

[0029]After extension is completed in this way, subsequently heat setting is performed. Heat setting performs 80-170 \*\* of for [ 2 to 600 seconds ] grade heat treatments at 100-160 \*\* preferably, it being feasible by a well-known means, and maintaining turgescence for the above-mentioned oriented film. The obtained oriented film can perform a cooling process, a rolling process, a printing job, dry laminate processing, a solution or melting coat processing, bag manufacture processing, deep drawing, box processing, tube processing, split processing, etc. if needed.

[0030]The shape of mold goods, such as a layered product obtained in this way, may be arbitrary, and a film, a sheet, a bottle, a pipe, a filament, a variant section extrusion thing, etc. are illustrated. A film, a

sheet, or a container obtained is useful like the above as various kinds of wrapping, such as common foodstuffs, a pouch-packed food, drugs, heavy chemicals, and agricultural chemicals.

[0031]By this invention, since melting mixing of EVOH of 25 to 50 % of the weight of water content and the water swelling laminar inorganic compound is carried out, it excels in the productivity of a resin composition and its molded product, and the resin composition obtained further shows the effect excellent in gas barrier property or appearance properties.

[0032]

[Example]An example is given to below and this invention is concretely explained to it. Especially, it means a weight reference that it is with the inside of an example "part" and "%", as long as there is no notice.

[0033]EVOH (ethylene content: -- 29-mol % and saponification degree:99.8-mol %.) of 35% of example 1 water content Melt-index (MI):8g/10 minute (210 \*\*, 2160g of load) 154 copy (100 copies (solid content) of EVOH(s)) is supplied to a twin screw extruder (30mmphi of ratio-of-length-to-diameter=40), After making EVOH into a molten state at the temperature of 80 \*\*, five copies of natural montmorillonites were added continuously there, temperature was set as 95 \*\*, and hydrous EVOH and natural montmorillonite were kneaded. The obtained resin composition was extruded and cut into strand shape after kneading, and the pellet was produced. Here, 35% of EVOH was adjusted with the following method. After having dissolved EVOH in the water-methanol mixed solvent (water/methanol =50/50 (weight ratio)), having produced 40% of paste, depositing this paste in chilled water and cutting to a pellet type, ion exchange water fully washed. The water content of this pellet resin was 55%, and it dried to 35% with the dryer, and it obtained EVOH of 35% of water content.

[0034]What performed vacuum drying at 60 \*\* and became 0.2% of water content about the above-mentioned pellet was supplied to the single screw extruder, in T-pressure die casting, the film was produced under conditions with an extrusion machine preset temperature of 220 \*\*, and a 30-micrometer film was obtained. The following evaluations were performed about the obtained film.

[0035](Oxygen transmittance) The obtained film was measured under the conditions of 20 \*\* and 80%RH with the equal pressure method (the MOCON method) using OXTRAN2/20 made from MOCON.

[0036](Appearance) In the obtained film, the diameter in 10 cm x 10 cm measured the number of foreign matters of 0.1 mm or more, and the following standard estimated.

O ... One or less piece O ... 2 - 5 piece x ... Six or more pieces were evaluated also about the productivity in the above-mentioned manufacturing method again.

[0037]In example 2 Example 1, EVOH Ethylene content:32-mol %, The degree of saponification: Except having changed the addition of natural montmorillonite into ten copies, and also having changed melting mixing temperature into 90 \*\*, it carried out to 99.8-mol %, MI:12g/EVOH for 10 minutes (210 \*\*, 2160g of load) similarly, and the same evaluation as Example 1 was performed to it.

[0038]In example 3 Example 1, EVOH Ethylene content:32-mol %, The degree of saponification: Except having changed water content to 45%, and having changed hydrous EVOH into 182 copies (100 copies (solid content) of EVOH(s)), and also having changed melting mixing temperature into 85 \*\*, it carried out to 99.8-mol %, MI:3g/EVOH for 10 minutes (210 \*\*, 2160g of load) similarly, and the same evaluation as Example 1 was performed to it.

[0039]In comparative example 1 Example 1, using EVOH (0% of water content) which does not contain water, it carried out similarly and the same evaluation as Example 1 was performed except having changed

the content of EVOH into 100 copies.

[0040]In comparative example 2 Example 1, except having changed the content of EVOH into 100 copies, and also having changed melting mixing temperature into 230 °C using EVOH (0% of water content) which does not contain water, it carried out similarly and the same evaluation as Example 1 was performed.

[0041]In comparative example 3 Example 1, EVOH Ethylene content:32-mol %, The degree of saponification : to 99.8-mol %, MI:3g/EVOH for 10 minutes (210 °C, 2160g of load). Except having changed the water content of EVOH to 60%, and having changed hydrous EVOH into 250 copies (100 copies (solid content) of EVOH(s)), and also having changed melting mixing temperature into 80 °C, it carried out similarly and the same evaluation as Example 1 was performed.

[0042]in comparative example 4 Example 1 -- EVOH (ethylene content: -- 32-mol %.) The degree of saponification: Except having carried out melting mixing of MI:3g/10 minute (210 °C, 2160g of load) 100 copy, and five copies of natural montmorillonites at 220 °C, having added ten copies of water there, and having obtained the resin composition 99.8-mol%, it carried out similarly and the same evaluation as Example 1 was performed. The result of an example and a comparative example is shown in Table 1.

[0043]

[Table 1]

productivity Oxygen transmittance the appearance (cc, 30 micrometer/m<sup>2</sup>, and day-atm) example 1 -- satisfactory -- processing 0.4 O<sup>2</sup> -- satisfactory -- processing 0.2 O<sup>2</sup> 3 -- satisfactory -- processing the 0.4 O comparative example 1 -- not processible --- ---. \*\* 2 -- satisfactory -- processing 1.2 x<sup>2</sup> 3 -- not processible --- --- \*\* 4 -- satisfactory -- processing 0.8 x[0044]

[Effect of the Invention]Since the manufacturing method of this invention is carrying out melting mixing of EVOH of 25 to 50 % of the weight of water content, and the water swelling laminar inorganic compound, it excels in the productivity of a resin composition and its molded product, and the resin composition obtained further shows the effect excellent in gas barrier property or appearance properties.

A film, a sheet, or a container is presented with these resin compositions, and they are useful as various kinds of wrapping, such as common foodstuffs, a pouch-packed food, drugs, heavy chemicals, and agricultural chemicals.

---

[Translation done.]